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This paper is part of the following report:

TITLE: Materials Research Society Symposium Proceedings. Volume 675.
Nanotubes, Fullerenes, Nanostructured and Disordered Carbon. Symposium
Held April 17-20, 2001, San Francisco, California, U.S.A.

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ADP012133 thru ADP012173

Lithium Insertion in Nanoporous Carbon Materials Produced from Carbides

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ABSTRACT

In this work, the results of a study of the lithium insertion process in nanoporous carbons (NPC) obtained from carbides (SiC, TiC, Mo_2C) by chlorination are presented. Lithium insertion was produced in the temperature range of 30-200 ^{0}C via the vacuum deposition and diffusion. The major analytical tools for study included nuclear reaction method and X-ray diffraction. Diffusion coefficients of lithium at this temperature interval were estimated. Possible mechanism of lithium diffusion is discussed. Investigation of phase composition of lithiated samples was carried out at room temperature. Phase composition is found to be dependent on the relationship between deposition and diffusion rates.

INTRODUCTION

In the past decade, significant research efforts have been focused on the search for suitable carbon materials as an alternative anode(s) for lithium rechargeable batteries. The main requirement to these materials is a high quantity of reversible lithium ion insertion. This property appears to be a function of the carbon network structure [1-2]. The structural variation of carbon materials also plays an important role in the stoichiometry and phase composition of the lithiated carbons.

In this paper, the process of lithium insertion in nanoporous carbons (NPC) obtained from carbides (SiC, TiC, Mo_2C) by chlorination is studied. These materials are of interest for their high-developed surface (total porosity is up to 70%) on which lithium deposition can take place and for high open nanoporosity that makes it possible to have enough value of lithium diffusion coefficient. The objectives of the study are to determine lithium diffusion mechanism and the factors that affect the stoichiometry and phase composition of lithium insertion in NPC.

EXPERIMENTAL

The samples used in this study (bulk NPC) were obtained through the temperature chlorinating process from an intermediate product prepared on the base carbide powders (SiC, TiC, Mo_2C). These materials have high total porosity up to 70% and nanoporosity about 50%. Their specific surface area is up to 1300 sm^2/ g. Pore sizes and value of graphitised fragments in bulk NPC under study depend on initial carbide powder [3]. So pore sizes are the largest in the npC< Mo_2C>B samples and are the smallest in the C< SiC>B ones. At he same time, total volume of ordered graphite fragments is the largest in the C< SiC>B samples.

Lithium insertion in the samples being studied was carried out by vacuum evaporation and subsequent diffusion at the temperatures ranging from 30 ^{o}C to 200 ^{o}C. The nuclear reaction

7Li(p,a)^{4}He was applied to measure the concentration profiles of lithium. Protons with energy Ep=1,1 MeV were used and α-particles were registered with Si surface barrier detector [4]. The total quantity of the evaporated lithium was monitored with Si sample. Is is known that in this temperature interval the diffusion of lithium into silicon does not practically take place [5]. In such a situation total quantity of evaporated Li is calculated by integration of the Li concentration profile. After cooling the lithiated samples were kept in an atmosphere of dry nitrogen.

The investigation of phase composition of the lithiated samples was performed by means of X-ray diffraction measurements using a " Geigerflex" D/max-Rc Rigaku diffractometer with a Co X-ray tube.

Samples were round with their diameter larger than their height. Therefore, to estimate lithium diffusion coefficient we have used the one-dimensional solution of diffusion equation obtained under the assumption that diffusing atoms do not interact with each other and the supply of lithium is infinite:

$$N(x) = N_0 erfc\left(\frac{x}{2\sqrt{Dt}}\right), \tag{1}$$

where erfc-complementary error function, N(x)- concentration at any point x, t-diffusion time, D-diffusion coefficient, N_0 –surface concentration of Li.

In some cases experimental lithium concentration profiles were given by the equation (1) with rather high accuracy (figure 1). This made it possible to determe lithium coefficient diffusion D_{Li} by the fitting of the experimental curve with one erfc function. If the fitting with one erfc was impossible, we determined D_{Li}, using the equation (1), in ten points of experimental curve and then calculated average value of diffusion constant ($<D_{Li}>$). As we will see below, the value of $<D_{Li}>$ may be used as the characteristic of the diffusion process.
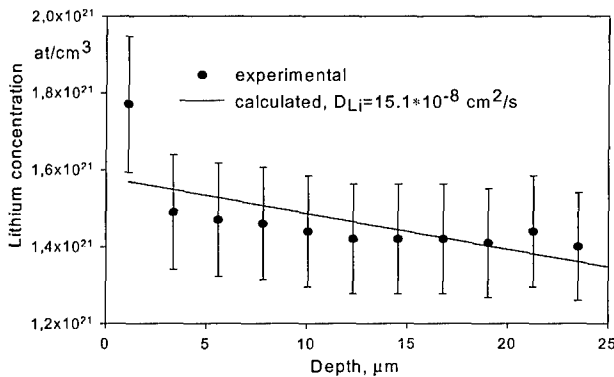

Figure 1. Lithium diffusion profile in the C<TiC>B sample .Temperature and time of diffusion are 80^{0}C and 10 min respectively. Straight line is the best fit of experimental results.

First of all we have carried out an investigation of the action of preliminary vacuum annealing on Li diffusion process. Table I shows $<D_{Li}>$ values in the samples under investigation

in the temperature range of 30 °C –100 °C before and after annealing at 200 °C during 4 hours. Diffusion process was conducted for 5 min. One can see that annealing leads to increase of $<D_{Li}>$ values. Effect of preliminary annealing depends on the type of samples under study and is more marked in the NPC with larger pore sizes. Moreover, a clear correlation is observed between the values of $<D_{Li}>$ and pore sizes: D_{Li} values are maximum in the C<Mo$_2$C>B samples and are minimum in the C<SiC>B ones. It is known that disordered carbon structure does not change at annealing temperature up to 1100°C [6], so the main result of annealing is the removal of adsorbed water. Taking into account this circumstance, increase of $<D_{Li}>$ after annealing can be connected with diffusion of lithium along the pore walls.

Table I. Values of diffusion coefficients in the samples of NPC prior to and after preliminary annealing. Diffusion time 5 min.

Sample	Number	T, ^{0}C	$<D_{Li}>*10^9$ cm^2/sec prior annealing	$<D_{Li}>*10^9$ cm^2/sec after annealing
C<SiC>B	2	30	2,5	6,6
C<TiC>B	32	30	2	12,6
C<Mo$_2$C>B	6	30	3,28	76
C<SiC>B	142	80	20,4	33
C<TiC>B	32	80	13,6	57
C<Mo$_2$C>B	6	80	200	101
C<SiC>B	21	100	10,3	21
C<TiC>B	44	100	2	400
C<Mo$_2$C>B	43	100	175	164

In separate experiments we studied Li insertion in the annealed samples at different diffusion process durations. Lithium diffusion processes have been performed at temperature 80°C during 5, 10 and 20 min. It turned out that the variation in the value of lithium diffusion coefficient, taking place as a function of diffusion time, depends on NPC type (Table II). From Table II we can see that increase of diffusion time from 10 min to 20 min results in decrease of D_{Li} in the C<SiC>B sample by a factor of approximately 6. At the same time in the C<TiC>B sample lithium diffusion coefficient is constant with variation of diffusion duration in this interval. Besides, for example, if at diffusion duration 20 min the diffusion coefficient values varied from $4,1*10^{-9}$ cm^2/sec for the C<SiC>B sample to $3,5*10^{-8}$ cm^2/sec for the C<TiC>B sample, almost by a factor of 9, then at diffusion duration 5 min., the values of diffusion coefficients for these samples differ from one another by a factor of only 1,5.

Table II. Diffusion coefficients at different durations of diffusion process. Diffusion temperature 80°C.

Sample	Number	$<D_{Li}>_*10^9$ cm^2/sec $t_{dif}=5'$	$<D_{Li}>_*10^9$ cm^2/sec $t_{dif}=10'$	$<D_{Li}>_*10^9$ cm^2/sec $t_{dif}=20'$
C<SiC>B	11	33,4	23	4,1
C<TiC>B	32	57	32	35
C<Mo$_2$SiC>B	6	101	–	–
	28	–	27	–
	28	101	–	–

It should be remembered that the insertion process of lithium into NPC samples is complicated. It includes lithium diffusion along pore walls and in graphitised fragments, accumulation of lithium in pores, intercalation Li in graphitised fragments and phase transition among intercalation stages. Certainly, all these processes are responsible for the value of Li diffusion coefficient. Therefore, we believe that the dependence of the diffusion coefficient on diffusion process duration can be related to intercalation or accumulation processes going simultaneously with diffusion process. It is possible that in the experiments with and without preliminary annealing Li diffusion process duration was short to manifest these processes. The results of XRD investigation of lithiated samples confirmed this assumption.

XRD phase composition examination was conducted in the samples preliminary treated at 300 °C for 70h to minimize the effects of water. Note that the formation of intercalation phase is observed mainly in the samples in which sufficient volume of the graphite-like fragments is available. This fact is in full accordance with results described in literature [7]. All the data presented below relate to the C<SiC>B samples.

To follow the structural changes during diffusion process, XRD study has been performed from both sides of the sample under investigation. It should be emphasized that Li insertion in the samples does not give a pure single-stage compound as determined by XRD patterns. Coexistence of several phases was always observed. Some of the results are shown in Figure 2. As one can see, intercalation phases LiC_6, LiC_{12} LiC_{24} and large volume of carbonate Li_2CO_3 and carbide Li_2C_2 phases are registered from the front side. At the same time from the back of the sample only small quantity of Li_2CO_3 and Li_2C_2 is seen. No evidence of Li_2CO_3 and Li_2C_2 existence was received when the sample was polished from the front side at the depth of 0,4 mm. However, the intercalation phases LiC_6, LiC_{12}, LiC_{24} are observed. Concentration profiles measured on both sides indicate that in this case high lithium gradient is available in the sample (figure 3). From this fact it transpires that the formation of Li_2CO_3 and Li_2C_2 phases strongly depends on Li concentration. We suppose that at first Li clusters arise when high concentration of lithium is available in pores and then clusters react with atmospheric CO_2 that is the cause of Li_2CO_3 formation. As for Li_2C_2, additional experiments are required to understand the mechanism of their formation.

It is evident that lithium filling pores will be dependent on the lithium deposition rate. We have examined the phase composition of the lithiated samples at different rates of Li deposition and diffusion. The total volume of carbonate and carbide phases decreased with the decrease of Li deposition rate and the increase of diffusion rate. As a result, it was stated that ratio between deposition and diffusion rates of lithium plays important role in the phase composition of lithiated samples. In order to exclude all possibility of formation Li_2C_2 and Li_2CO_3 phases we

have used the impuls deposition of lithium. The duration of impuls (5 min.) was rather less than the time interval brtween impulses (3h). Thanks to this we have produced the samples up to a thickness of about 0,6 mm uniformly impregnated by lithium and containing intercalation phases only.
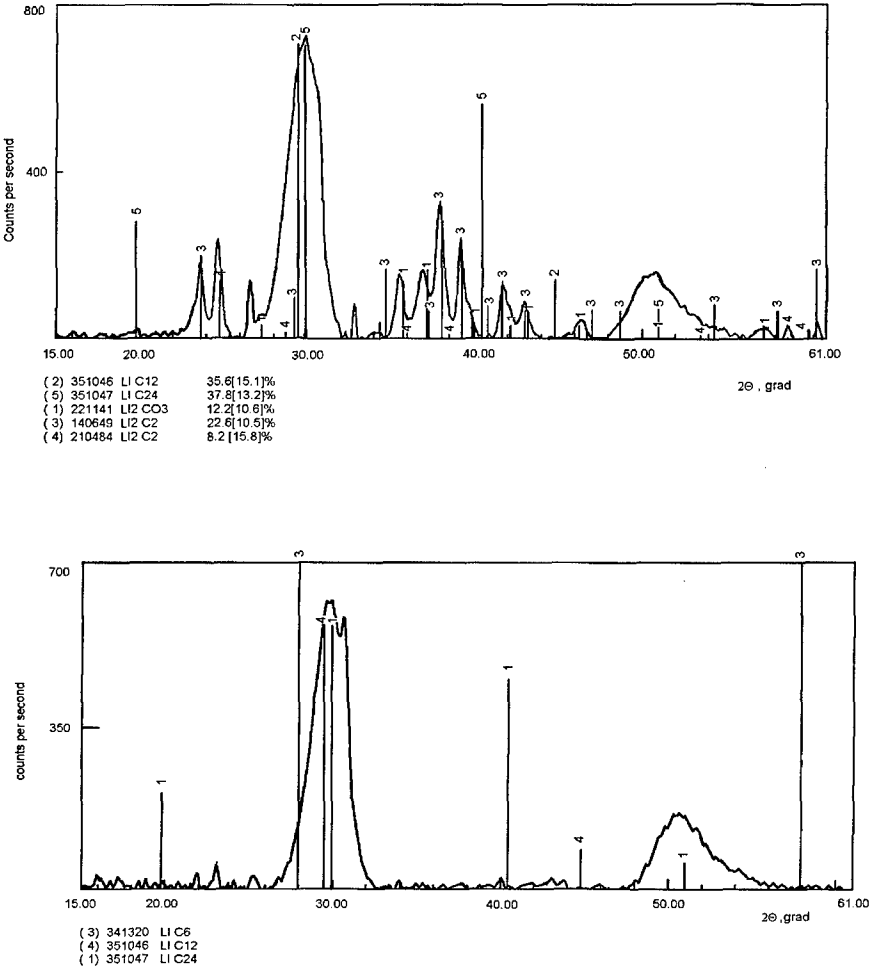

(2)	351046	LI C12	35.6[15.1]%
(5)	351047	LI C24	37.8[13.2]%
(1)	221141	LI2 CO3	12.2[10.6]%
(3)	140649	LI2 C2	22.6[10.5]%
(4)	210484	LI2 C2	8.2 [15.8]%

(3)	341320	LI C6
(4)	351046	LI C12
(1)	351047	LI C24

Figure 2. X-ray diffractional patterns of lithiated C<SiC>B sample for front side (a) and back side (b). Diffusion time 30 houres.
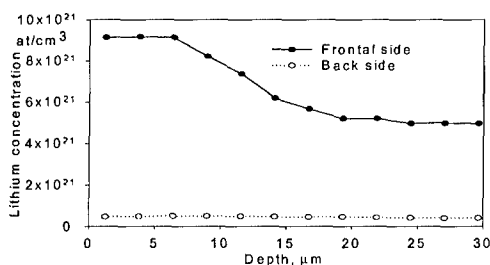
Figure 3. Concentration profiles measured on different side of sample #2 C<SiC>B

CONCLUSION

We have investigated the process of Li insertion in nanoporous carbons at the temperature range of 30-200 ^{0}C. The diffusion process was studied at different deposition and diffusion rates.

A comparison of diffusion processes in different NPC allows to conclude that the main mechanism of diffusion is lithium diffusion along pore walls. As a result of lithium diffusion process investigations in different NPC samples with and without preliminary annealing, it is stated that the value of lithium diffusion coefficient depends on the size of pores and their physical state. Values of D_{Li} in the above-mentioned temperatures vary for different samples in the range $10^{-9} - 10^{-7}$ cm^2/s. The value of lithium diffusion coefficient depends on the diffusion process duration. It is elucidated that such behavior <D_{Li}> reflects the different processes that occur in series during the entire insertion process: Li diffusion over pore walls, accumulation of Li in pores giving rise to Li clusters and the formation of intercalation phases.

Intercalation phases LC$_6$, LiC$_{12}$, LiC$_{24}$ and LiC$_{40}$ were observed. Besides, Li$_2$C$_2$ and Li$_2$CO$_3$ phases were registered in some cases. It was stated that the correlation between the diffusion rate and the evaporation rate is responsible for the phase composition. Based of this fact the process technology conditions for producing of lithiated samples without lithium carbide and carbonate were found. The samples up to a thickness of about 0,6 mm uniformly impregnated by lithium and containing intercalation phases only were produced.

The studies were carried out on NPC samples developed and produced in collaboration with Skeleton Technologies Group.

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